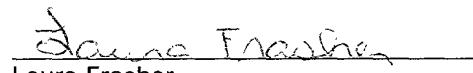


JOINT INVENTORS

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Laura Frasher

APPLICATION FOR UNITED STATES LETTERS PATENT

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

Be it known that we, Geun Su Lee a citizen of the Republic of
Korea, residing at #103-302 Samick Apt., Bubal-eub, Shinha-ri, Ichon-shi,
Kyoungki-do 467-860, Republic of Korea and Jae Chang Jung, a citizen of
the Republic of Korea, residing at #107-1304 Hyundai Apt., Sadong-ri,
Daewol-myeon, Ichon-shi, Kyoungki-do 467-850, Republic of Korea and Ki
Soo Shin, a citizen of the Republic of Korea, residing at #307-1301 Kisan
Apt., Yatop-2-dong, Bundang-gu, Sungnam-shi, Kyoungki-do 463-070,
Republic of Korea, have invented a new and useful PHOTORESIST
MONOMERS, POLYMERS, THEREOF AND PHOTORESIST COMPOSITIONS
CONTAINING THE SAME, of which the following is a specification.

**PHOTORESIST MONOMERS, POLYMERS THEREOF AND
PHOTORESIST COMPOSITIONS CONTAINING THE SAME**

BACKGROUND

5 Technical Field

Photoresist monomers, polymers thereof and photoresist compositions containing the same are disclosed. In particular, photoresist monomers suitable for a photolithography process using DUV (deep ultraviolet) light sources, particularly VUV (vacuum ultraviolet : 157nm) in fabricating a minute circuit for a high 10 integration semiconductor device, photoresist polymers thereof, photoresist compositions containing the same, and preparation processes are also disclosed.

Description of the Related Art

15 In general, a useful photoresist for ArF and VUV has a variety of desired characteristics, such as low light absorbance at the wavelength of 193nm and 157nm, excellent etching resistance, and excellent adhesiveness to a wafer. In addition, a photoresist should be easily developable in a commercially readily available developing solution, such as 2.38wt% and 2.6wt% aqueous tetramethylammonium hydroxide (TMAH) solution.

20 Recently, much research has been conducted on resins having a high transparency at the wavelength of 248nm and 193nm and dry etching resistance similar to novolac resin. However, most of the photoresists are not suitable for VUV due to their poor transmittance at 157nm wavelength.

25 Photoresists containing fluorine have good transmittance at these wavelengths. Unfortunately, most photoresists containing fluorine with a polyethylene, polystyrene or polyacrylate polymer backbone have weak etching resistance, low solubility in an aqueous TMAH solution and poor adhesiveness to the silicon wafer. In addition, these photoresists are difficult to mass-produce and are expensive.

30 On the other hand, photoresists containing fluorine with alicyclic polymer or maleicanhydride-norbonene polymer backbone have good adhesiveness to the silicon wafer, low light absorbance at the wavelength of 157nm and excellent etching resistance compared to photoresists with polyacrylate backbone.

SUMMARY OF THE DISCLOSURE

Accordingly, novel photoresist monomers, polymers thereof and photoresist compositions containing the same that can be used for a light sources such as ArF (193nm) and VUV (157nm) are disclosed.

5 A process for forming a photoresist pattern using the photoresist compositions described above and a semiconductor element produced by using the process described above are also disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

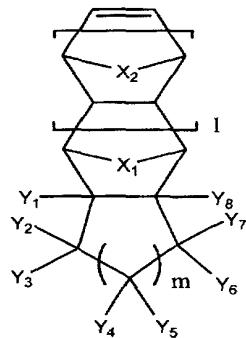
10 Figure 1 is a photograph of a photoresist pattern obtained from Example 9;
Figure 2 is a photograph of a photoresist pattern obtained from Example 10;
Figure 3 is a photograph of a photoresist pattern obtained from Example 11;
Figure 4 is a photograph of a photoresist pattern obtained from Example 12;
and

15 Figure 5 is a VUV spectrum for a photoresist composition obtained from Example 9.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

20 First, a photoresist monomer is disclosed that is represented by following Formula 1:

Formula 1



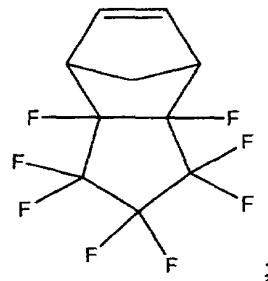
25 wherein, X₁ and X₂ individually are selected from the group consisting of C₁-C₁₀alkylene, O and S;

Y₁, Y₂, Y₃, Y₄, Y₅, Y₆, Y₇ and Y₈ individually are selected from the group consisting of halogen and an alkyl partially or wholly substituted with halogen, more preferably F, Cl, Br, I or CF₃; and

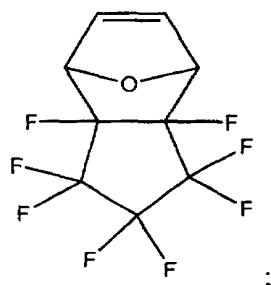
l and *m* are individually integers from 0 to 3.

5 Some of preferred photoresist monomers are disclosed, but are not limited to, as following Formulas 1a to 1d:

Formula 1a

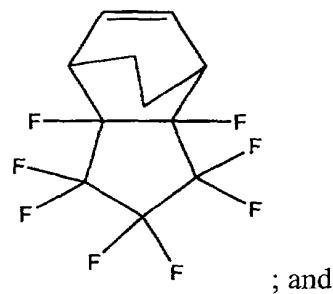


Formula 1b

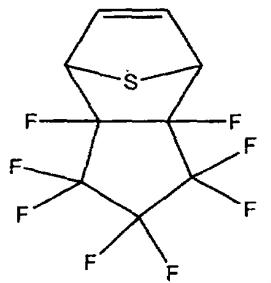


10

Formula 1c



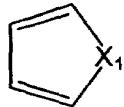
Formula 1d



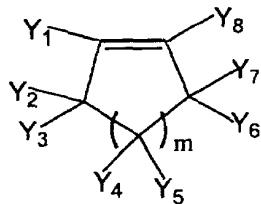
The compound of above Formula 1, can be obtained by reacting cycloalken of following Formula 2 and cycloalken substituted with halogen or CF_3 of following

5 Formula 3.

Formula 2



Formula 3



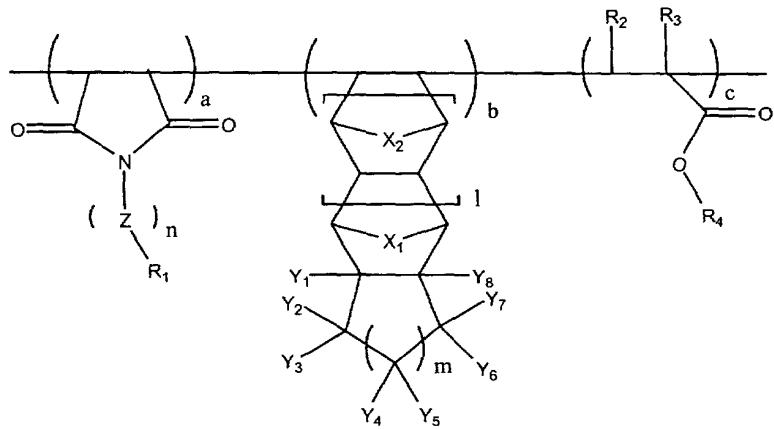
10 wherein, X_1 is selected from the group consisting of $(\text{C}_1\text{-C}_{10})\text{alkylene}$, O and S;

Y_1 , Y_2 , Y_3 , Y_4 , Y_5 , Y_6 , Y_7 and Y_8 individually are selected from the group consisting of halogen and an alkyl partially or wholly substituted with halogen, more preferably F, Cl, Br, I or CF_3 ; and

15 m is integer from 0 to 3.

In addition, a repeating unit is represented by following Formula 4 comprising the compound of Formula 1 as a comonomer and photoresist polymer comprising the repeating unit of Formula 4.

Formula 4



wherein, R₁, R₂ and R₃ individually are selected from the group consisting of H, halogen, (C₁-C₂₀) alkyl, (C₁-C₂₀) alkyl with halogen substituent(s), (C₁-C₂₀) alkyl containing an ether group (-O-), and (C₁-C₂₀) alkyl with halogen substituent(s) and containing an ether group;

5 R₄ is an acid labile protecting group;

X₁ and X₂ individually are selected from the group consisting of (C₁-C₁₀)alkylene, O and S;

10 Y₁, Y₂, Y₃, Y₄, Y₅, Y₆, Y₇ and Y₈ individually are selected from the group consisting of halogen and alkyl partially or wholly substituted with halogen;

Z is O or S;

15 l and m are individually integers from 0 to 3;

n is 0 or 1; and

a : b : c falls within the ranges 0-60mol% : 5-80mol% : 0-90mol%.

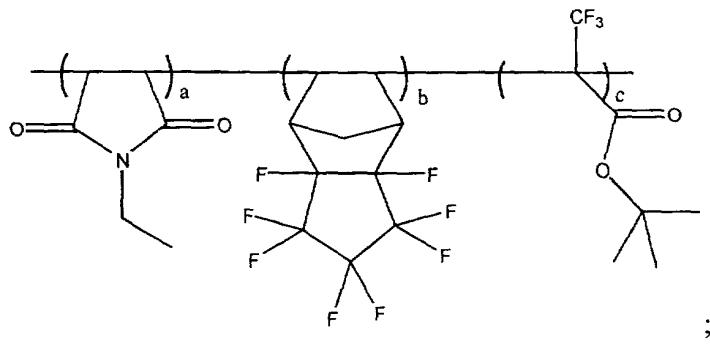
More preferably, above R₁, R₂ and R₃ individually are selected from the group consisting of H, F, (C₁-C₂₀) alkyl, (C₁-C₂₀) perfluoroalkyl, (C₁-C₂₀) alkyl containing an ether group, (C₁-C₂₀) perfluoroalkyl containing an ether group, (C₁-C₂₀) alkyl partially substituted with F, and (C₁-C₂₀) alkyl partially substituted with F and containing an ether group, and, above Y₁, Y₂, Y₃, Y₄, Y₅, Y₆, Y₇ and Y₈ individually are selected from the group consisting of F, Cl, Br, I and CF₃.

And the acid labile protecting group can be any of known protecting groups which prevent the compound from dissolving in an alkaline developing solution. However, under the presence of acid, the acid labile group is substituted with acid, 25 thereby making the compound soluble to the alkaline solution. Some of

conventional acid labile protecting groups are disclosed in US 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0789 278 (Aug 13, 1997), US 6,132,926 (Oct 17, 2000), US 6,143,463 (Nov 7, 2000), US 6,150,069 (Nov 21, 2000), US 6,180,316 B1 (Jan 30, 5 2001), US 6,225,020 B1 (May 1, 2001), US 6,235,448 B1 (May 22, 2001) and US 6235447 B1 (May 22, 2001). Acid labile protecting groups of the present invention are preferably selected from the group consisting of tert-butyl, tetrahydropyran-2-yl, 2-methyl tetrahydropyran-2-yl, tetrahydrofuran-2-yl, 2-methyl tetrahydrofuran-2-yl, 1-methoxypropyl, 1-methoxy-1-methylethyl, 1-ethoxypropyl, 1-ethoxy-1-methylethyl, 10 1-methoxyethyl, 1-ethoxyethyl, tert-butoxyethyl, 1-isobutoxyethyl and 2-acetylmenth-1-yl.

Some of preferred repeating unit of above Formula 4 are disclosed, but are not limited to, as following Formulas 4a to 4d:

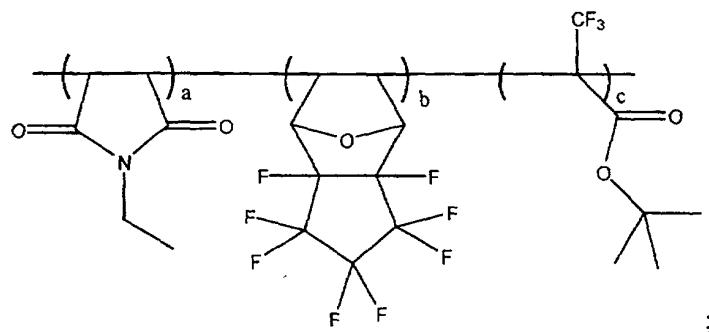
Formula 4a



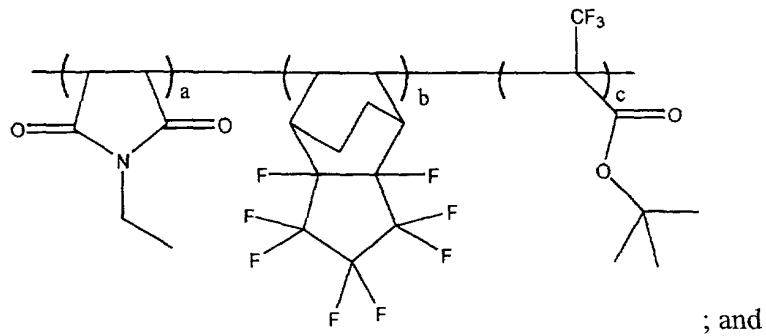
15

;

Formula 4b

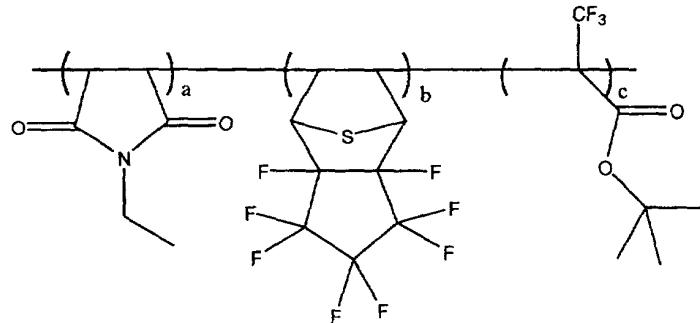


Formula 4c



; and

Formula 4d



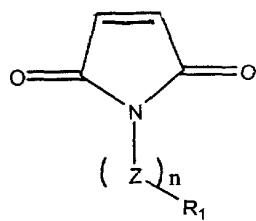
5 wherein, the ratio a : b : c falls within the ranges 0-60mol% : 5-80mol% : 0-90mol%.

The process for preparing of a photoresist polymer comprising the repeating unit of Formula 4 will now be explained in more detail.

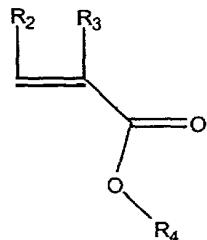
10 The disclosed repeating unit of above Formula 4 can be prepared by radical-polymerization the compound of above Formula 1 and optionally maleimide derivative of following Formula 5 or acrylate derivative of following Formula 6. The process comprises:

- (a) admixing (i) a compound of Formula 1 and optionally (ii) the compound of Formula 5 or the compound of Formula 6; and
- 15 (b) adding a polymerization initiator into the resultant of step (a) to obtain a repeating unit of Formula 4.

Formula 5



Formula 6



5 wherein, R_1 , R_2 and R_3 individually are selected from the group consisting of H, halogen, (C_1-C_{20}) alkyl, (C_1-C_{20}) alkyl with halogen substituent(s), (C_1-C_{20}) alkyl containing an ether group, and (C_1-C_{20}) alkyl with halogen substituent(s) and containing an ether group;

R_4 is an acid labile protecting group;

10 Z is O or S; and

n is 0 or 1.

More preferably, above R_1 , R_2 and R_3 individually are selected from the group consisting of H, F, (C_1-C_{20}) alkyl, (C_1-C_{20}) perfluoroalkyl, (C_1-C_{20}) alkyl containing an ether group, (C_1-C_{20}) perfluoroalkyl containing an ether group, (C_1-C_{20}) alkyl 15 partially substituted with F, and (C_1-C_{20}) alkyl partially substituted with F and containing an ether group.

And the acid labile protecting group is same as mentioned above.

In the above process, radical polymerization is carried out by bulk polymerization or solution polymerization.

20 In case it is carried out by solution polymerization, the organic solvents suitable for polymerization can be cyclohexanone, cyclopentanone, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, dioxane, methylethylketone, benzene, toluene, xylene or mixtures thereof.

The polymerization initiators can be any conventional one, preferably a radical polymerization initiators such as 2,2'-azobisisobutyronitrile(AIBN), benzoyl peroxide, acetyl peroxide, lauryl peroxide, tert-butyl peracetate or di-tert-butyl peroxide.

On the other hand, the repeating unit can be prepared by using metal catalyst
5 as disclosed in WO 96/37526 (Nov 28, 1996).

More preferably, after polymerization, the repeating unit is subject to crystallization and/or purification by using diethyl ether, petroleum ether, alcohol, water or mixtures thereof.

A photoresist polymer comprises the above repeating unit in the main chain
10 and further comprises other comonomers or additives as occasion demands.

In addition, a photoresist composition comprises (i) a photoresist polymer described above; (ii) a photoacid generator; and (iii) an organic solvent.

Any of conventional photoacid generator, which is able to generate acids when it is exposed to light, can be used. Some of conventional photoacid generator are
15 disclosed in US 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0789 278 (Aug 13, 1997) and US 6,132,926 (Oct 17, 2000), US 6,143,463 (Nov 7, 2000), US 6,150,069 (Nov 21, 2000), US 6,180,316 B1 (Jan 30, 2001), US 6,225,020 B1 (May 1, 2001), US 6,235,448 B1 (May 22, 2001) and US 6235447 B1 (May 22, 2001).

20 Preferred photoacid generators have relatively low light absorbance in the wavelength of 157nm and 193nm. More preferred photoacid generator is phthalimidotrifluoromethane sulfonate, dinitrobenzyltosylate, n-decyl disulfone, naphthylimido trifluoromethane sulfonate or mixtures thereof.

The photoacid generator can further comprise a compound selected from the
25 group consisting of diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, dibutylnaphthylsulfonium triflate and mixtures thereof.

30 Typically, the amount of photoacid generator is from about 0.05 to about 10% by weight of the photoresist polymer employed. It has been found that when the photoacid generator is used in the amount less than about 0.05%, it lowers photosensitivity of the photoresist composition, and when the photoacid generator is

used in the amount greater than about 10%, it results in a poor pattern formation due to its high absorption.

On the other hand, any of conventional organic solvent can be employed for this invention and some of the conventional one are also disclosed in the documents 5 described above. Preferred organic solvents for photoresist composition is methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, propylene glycol methyl ether acetate, cyclohexanone, 2-heptanone, ethyl lactate or mixture thereof.

The amount of organic solvent ranges from about 500 to about 2000% by weight of the photoresist polymer to coat the photoresist in a wanted thickness. It 10 has been found that when the organic solvent is used in the amount of about 1000wt%, a thickness of the photoresist is about 0.25μm.

A process for forming a photoresist pattern comprises:

- (a) coating the photoresist composition described above on a substrate to form a photoresist film;
- 15 (b) exposing the photoresist film to light; and
- (c) developing the exposed photoresist film to obtain a photoresist pattern.

The process for forming the photoresist pattern can further include a soft baking which is preformed before the step (b) and/or a post baking step which is preformed after the step (b). Preferably, the soft and post baking steps are performed 20 at temperature in the range of from about 70 to about 200°C.

Exemplary light sources which are useful for forming the photoresist pattern include not only VUV but also ArF, KrF, E-beam, EUV or ion beam. Preferably, the irradiation energy in the step (b) is in the range of from about 1mJ/cm² to about 100 mJ/cm².

25 On the other hand, the step (c) can be performed in alkaline developing solution which is preferably TMAH aqueous solution with a concentration ranging from about 0.01 to about 5wt%.

In addition, a semiconductor device can be manufactured using the photoresist compositions described above.

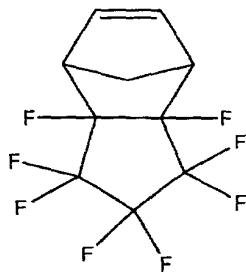
30 The disclosed monomers, polymers and photoresist compositions will now be described in more details by referring to examples below, which are not intended to be limiting.

I. Preparation of Photoresist Monomers

Example 1--Synthesis of Compound of Formula 1a

Cyclopentadiene(1mole) and 1,2,2,3,3,4,4,5-octafluorocyclopentene(1mole) were stirred for about 1 hour at about -10°C and then the temperature was slowly raised to reach room temperature. At the same temperature, the reaction was proceeded for about 10 hours, thereby obtaining the following Formula 1a (yield 98%).

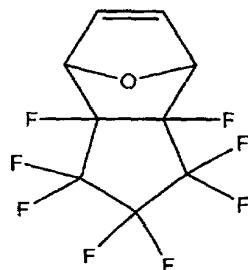
Formula 1a



Example 2--Synthesis of Compound of Formula 1b

Furan(1mole) and 1,2,2,3,3,4,4,5-octafluorocyclopentene(1mole) were stirred for about 1 hour at about -10°C and then the temperature was slowly raised to reach room temperature. At the same temperature, the reaction was proceeded for about 10 hours, thereby obtaining the following Formula 1b (yield 98%).

Formula 1b

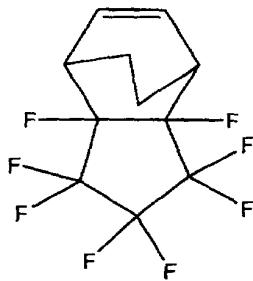


15

Example 3--Synthesis of Compound of Formula 1c

Cyclohexadiene(1mole) and 1,2,2,3,3,4,4,5-octafluorocyclopentene(1mole) were stirred for about 1 hour at about -10°C and then the temperature was slowly raised to reach room temperature. At the same temperature, the reaction was proceeded for about 10 hours, thereby obtaining the following Formula 1c (yield 98%).

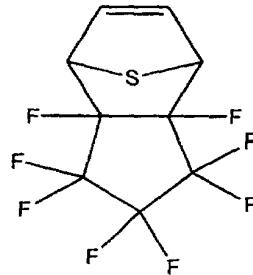
Formula 1c



Example 4--Synthesis of Compound of Formula 1d

Thiopene(1mole) and 1,2,2,3,3,4,4,5-octafluorocyclopentene(1mole) were 5 stirred for about 1 hour at about -10°C and then the temperature was slowly raised to reach room temperature. At the same temperature, the reaction was proceeded for about 10 hours, thereby obtaining the following Formula 1d (yield 98%).

Formula 1d

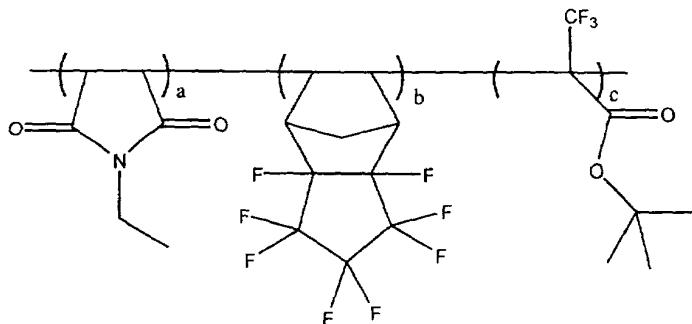


10 **II. Preparation of Photoresist Polymers**

Example 5--Synthesis of Compound of Formula 4a

To 10mL of tetrahydrofuran was added ethylmaleimide(0.01mole), the compound of Formula 1a obtained from Example 1(0.01mole), tert-butyl-2-(trifluoromethyl)-acrylate(0.02mole) and AIBN(0.4g), and the resulting solution was 15 reacted at about 65°C for about 10 hours. Thereafter, a polymer was precipitated and filtered in diethyl ether solution, thereby obtaining the following Formula 4a (yield : 51%).

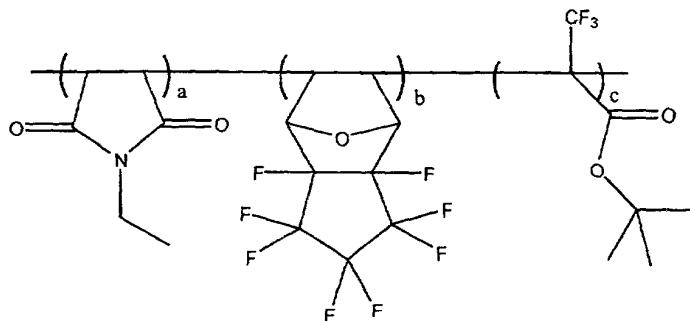
Formula 4a



Example 6--Synthesis of Compound of Formula 4b

To 10mL of tetrahydrofuran was added ethylmaleimide(0.01mole), the
5 compound of Formula 1b obtained from Example 2(0.01mole), tert-butyl-2-(trifluoromethyl)-acrylate(0.02mole) and AIBN(0.4g), and the resulting solution was reacted at about 65°C for about 10 hours. Thereafter, a polymer was precipitated and filtered in diethyl ether solution, thereby obtaining the following Formula 4b (yield : 51%).

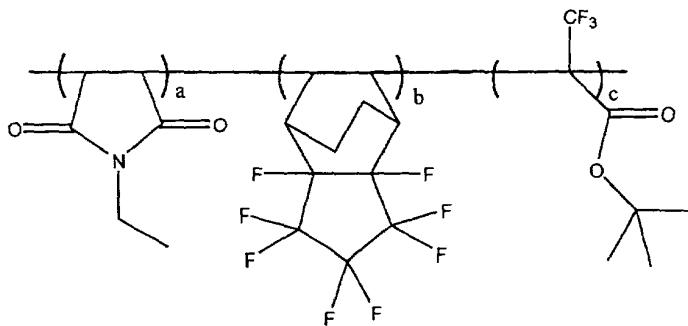
10 Formula 4b



Example 7--Synthesis of Compound of Formula 4c

To 10mL of tetrahydrofuran was added ethylmaleimide(0.01mole), the
15 compound of Formula 1c obtained from Example 3(0.01mole), tert-butyl-2-(trifluoromethyl)-acrylate(0.02mole) and AIBN(0.4g), and the resulting solution was reacted at about 65°C for about 10 hours. Thereafter, a polymer was precipitated and filtered in diethyl ether solution, thereby obtaining the following Formula 4a (yield : 51%).

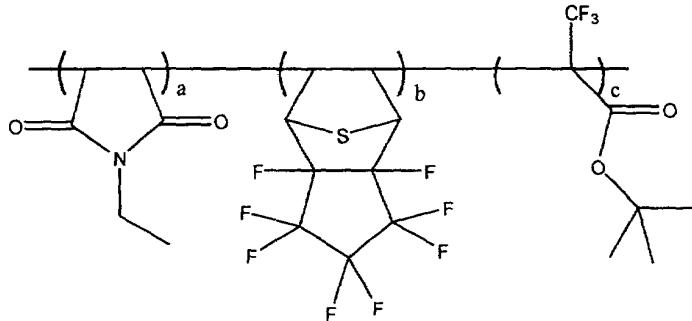
Formula 4c



Example 8--Synthesis of Compound of Formula 4d

To 10mL of tetrahydrofuran was added ethylmaleimide(0.01mole), the 5 compound of Formula 1d obtained from Example 4(0.01mole), tert-butyl-2-(trifluoromethyl)-acrylate(0.02mole) and AIBN(0.4g), and the resulting solution was reacted at about 65°C for about 10 hours. Thereafter, a polymer was precipitated and filtered in diethyl ether solution, thereby obtaining the following Formula 4d (yield : 51%).

10 Formula 4d



III. Preparation of Photoresist Compositions and Formation of Patterns

Example 9--Preparation of photoresist compositions and formation of patterns(1).

15 To 20g of propylene glycol methyl ether acetate(PGMEA) was added 2g of the compound of Formula 4a obtained from Example 5, 0.024g of phthalimidotrifluoromethane sulfonate, and 0.06g of triphenylsulfonium triflate. The polymer was precipitated and filtered in 0.20μm filter to obtain a photoresist composition.

20 The photoresist composition thus prepared was spin-coated on silicon wafer to form a photoresist film, and soft-baked at about 130°C for about 90 seconds. After

baking, the photoresist was exposed to light using a KrF laser exposer, and then post-baked at about 130°C for about 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 0.13μm L/S pattern (see Figure 1).

5 Example 10--Preparation of photoresist compositions and formation of patterns(2).

To 20g of propylene glycol methyl ether acetate(PGMEA) was added 2g of the compound of Formula 4b obtained from Example 6, 0.024g of phthalimidotrifluoromethane sulfonate, and 0.06g of triphenylsulfonium triflate.

10 The polymer was precipitated and filtered in 0.20μm filter to obtain a photoresist composition.

The photoresist composition thus prepared was spin-coated on silicon wafer to form a photoresist film, and soft-baked at about 130°C for about 90 seconds. After baking, the photoresist was exposed to light using a KrF laser exposer, and then post-baked at about 130°C for about 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 0.13μm L/S pattern (see Figure 2).

15 Example 11--Preparation of photoresist compositions and formation of patterns(3).

20 To 20g of propylene glycol methyl ether acetate(PGMEA) was added 2g of the compound of Formula 4c obtained from Example 7, 0.024g of phthalimidotrifluoromethane sulfonate, and 0.06g of triphenylsulfonium triflate. The polymer was precipitated and filtered in 0.20μm filter to obtain a photoresist composition.

25 The photoresist composition thus prepared was spin-coated on silicon wafer to form a photoresist film, and soft-baked at about 130°C for about 90 seconds. After baking, the photoresist was exposed to light using a KrF laser exposer, and then post-baked at about 130°C for about 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 0.13μm L/S pattern (see Figure 3).

Example 12--Preparation of photoresist compositions and formation of patterns(4).

To 20g of propylene glycol methyl ether acetate(PGMEA) was added 2g of the compound of Formula 4d obtained from Example 8, 0.024g of 5 phthalimidotrifluoromethane sulfonate, and 0.06g of triphenylsulfonium triflate. The polymer was precipitated and filtered in 0.20 μ m filter to obtain a photoresist composition.

The photoresist composition thus prepared was spin-coated on silicon wafer to form a photoresist film, and soft-baked at about 130°C for about 90 seconds. After 10 baking, the photoresist was exposed to light using a KrF laser exposer, and then post-baked at about 130°C for about 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 0.13 μ m L/S pattern (see Figure 4).

Experimental example--Investigation of a light absorbance at 157nm wavelength

A light absorbance of photoresist composition obtained from Example 9 coated in a thickness of about 2500 \AA was shown by VUV spectrum of Figure 5. According to Figure 5, the light absorbance of photoresist composition obtained from Example 9 at 157nm wavelength is 0.22 which is only below half of the light 20 absorbance of usual KrF or ArF photoresist. Therefore, the conventional photoresist composition should be coated below a thickness of 700 \AA in order to satisfy a light transmittance when it used in the photolithography employing the light of 157nm. While a photoresist pattern can be formed successfully using a photoresist 25 composition of this present invention though it coated over a thickness of about 1000 \AA because of excellent transmittance at 157nm wavelength. In this way, the present invention can obtain a more increased etching resistance because photoresist film can be formed sufficient thickness.

The above Experimental Example implies that photoresist composition comprising photoresist polymer of this present invention can be used in a 30 photolithography employing the light of 157nm because of excellent transmittance at 157nm wavelength. In addition, from Examples 9 to 12, it is ascertained that the

photoresist composition comprising the photoresist polymer according to the present invention has effective physical property as a photoresist.

As discussed earlier, a photoresist pattern having excellent durability, etching resistance, and developable property can be formed successfully by employing the photoresist composition of this present invention. And the photoresist composition of this present invention can be used in forming a minute pattern below 1G DRAM as well as 4G and 16G. Moreover, the photoresist polymer of this present invention has a low light absorbance at the 157nm wavelength, and thus is suitable for a photolithography using VUV.

10